Current and emerging techniques for DNAPL site characterization

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- Challenges to DNAPL site characterization
- Site Characterization Methods
  - Qualitative versus Quantitative data
- Current and emerging techniques
  - Examples from chlorinated solvents and coal tar sites
- Guidance documents
Challenges to DNAPL site characterization
Early stage mass distribution

DNAPL Zone

VOC >90%

Plume Zone

VOC <10%
Mass distribution dynamics

**Legend:**
- Reversible phase transfer
- Irreversible phase transfer

<table>
<thead>
<tr>
<th>Source</th>
<th>Plume</th>
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<tbody>
<tr>
<td>Low Permeability</td>
<td>Transmissive</td>
</tr>
<tr>
<td>Vapor</td>
<td><img src="image" alt="Diagram of vapor movement" /></td>
</tr>
<tr>
<td>DNAPL</td>
<td><img src="image" alt="Diagram of DNAPL movement" /></td>
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<tr>
<td>Aqueous</td>
<td><img src="image" alt="Diagram of aqueous movement" /></td>
</tr>
<tr>
<td>Sorbed</td>
<td><img src="image" alt="Diagram of sorbed movement" /></td>
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Site Characterization Methods
Qualitative versus Quantitative
Qualitative versus Quantitative Data

- The first category provides **qualitative**, dense spatial data and generates decision-quality data that guides future investigations
  - Often with higher detection limits over a preset value
  - Generally of lower cost, produce vertical profiles of real-time data
  - Examples of such "decision quality" methods are laser-induced fluorescence [LIF] profiling and membrane interface probing [MIP]

- The second category of technologies that are **quantitative** and typically compound-specific
  - They provide precise data that have low detection limit
  - Tend to be higher cost with longer turnaround times that preclude on-site decision making
  - Examples include the use of fully cored boreholes (and associated sub-sampling) and high-resolution multilevel well completions
Current and emerging techniques
Current tools and techniques

<table>
<thead>
<tr>
<th>Direct measurement</th>
<th>Indirect measurement</th>
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<tbody>
<tr>
<td>Visual observation</td>
<td>Site history</td>
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<tr>
<td>Enhanced visual methods</td>
<td>Soil (partitioning threshold)</td>
</tr>
<tr>
<td>Drive point tools</td>
<td>Groundwater (Effective solubility)</td>
</tr>
</tbody>
</table>

- **No SINGLE technique available to characterise a DNAPL site**
- **Typically, resolution decreases with depth and hydrogeological complexity and may constrain the selection, application and performance assessment of remediation technologies**
Direct: Visual observation

From soil and rock core or grab samples
- Rare at chlorinated solvent sites
- Common at coal tar sites

Samples recovered during from pumping from wells
- Typically requires pooled DNAPL
Direct: Enhanced Visual

After Mercer and Cohen (1993)

Legend

- **Correct determination of NAPL presence or absence**
- **NAPL suspected present when it was present**
- **NAPL suspected present when it was absent**
- **No NAPL present**
- **Incorrect determination**

Number of samples:

- Unaided visual
- Soil-water shake test
- UV fluorescence
- Hydrophobic dye shake test
- Centrifugation of the dye shake test
Dye shake test using Sudan IV

Individual sample

Depth profile
FACT NAPL FLUTe
(Flexible liner underground everting membrane)

## Direct drive tools summary

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Video imaging [GeoVis]</td>
<td>• Can be coupled with lithological logs</td>
<td>• Limited by lithology</td>
</tr>
<tr>
<td></td>
<td>• Data easy to interpret in suitable soil matrix</td>
<td>• Transparent DNAPL not visible</td>
</tr>
<tr>
<td></td>
<td>• Limited by lithology</td>
<td>• Clays may smear the camera window</td>
</tr>
<tr>
<td>Membrane Interface Probe [MIP]</td>
<td>• Can be coupled with lithological logs</td>
<td>• Limited by lithology</td>
</tr>
<tr>
<td></td>
<td>• Range of detectors [FID, PID, ECD]</td>
<td>• Semi-quantitative</td>
</tr>
<tr>
<td></td>
<td>• Excellent screening level data</td>
<td>• High operator skill required</td>
</tr>
<tr>
<td>Laser Induced fluorescence [LIF]</td>
<td>• Can be coupled with lithological logs</td>
<td>• Limited by lithology</td>
</tr>
<tr>
<td></td>
<td>• Simple detection methodology</td>
<td>• Semi-quantitative</td>
</tr>
<tr>
<td></td>
<td>• Excellent screening level data</td>
<td>• False positives may be detected</td>
</tr>
<tr>
<td>Dye-LIF</td>
<td>• Can be coupled with lithological logs</td>
<td>• Limited by lithology</td>
</tr>
<tr>
<td></td>
<td>• Applicable to non-fluorescing compounds</td>
<td>• Still under development</td>
</tr>
<tr>
<td></td>
<td>• Excellent screening level data</td>
<td></td>
</tr>
<tr>
<td>TarGOST</td>
<td>• Can be coupled with lithological logs</td>
<td>• Limited by lithology</td>
</tr>
<tr>
<td></td>
<td>• Applicable to coal tar compound</td>
<td>• Only applicable to coal tar compounds</td>
</tr>
<tr>
<td></td>
<td>• Excellent screening level data</td>
<td></td>
</tr>
</tbody>
</table>
ASTM D7352 - 07 Standard Practice for Direct Push Technology for Volatile Contaminant Logging with the Membrane Interface Probe (MIP)
Laser Induced Fluorescence
Tar-specific Green Optical Screening Tool, Tar-GOST ®

% Reference Emitter Response =
\[ \frac{\text{\(\sum\) area under SAMPLE fluorescence peaks}}{\text{\(\sum\) area under REFERENCE fluorescence peaks}} \]

\[ \frac{\text{Area under SAMPLE scatter peak}}{\text{Area under REFERENCE scatter peak}} \]
Converting LIF response to DNAPL saturation
Indirect: Site history

- Previous investigations
- Aerial photographs
- Building plans
- Former lagoons, USTs, drains
- Production records
- Employee interviews
- Sale records
Soil core data
Indirect: Soil partitioning threshold

\[ C_D = \frac{S_r \phi \rho_N 10^6}{\rho_b} + C^T \]

Where:

- \( C_D \) is soil concentration (mg/kg) corresponding to threshold DNAPL saturation
- \( S_r \) is threshold DNAPL saturation
- \( \phi \) is the porosity
- \( \rho_N \) is DNAPL density (g/cc)
- \( \rho_b \) is dry soil bulk density (g/cc)
- \( C^T \) is amount of contaminant (mg/kg) in the samples, including aqueous, vapour and sorbed

Kueper and Davies, 2009
Indirect:

Theoretical pore water concentration

\[ C_w = \frac{C_t \rho_b}{(K_d \rho_b + n)} \]

- \( C_w \) is the pore water concentration (mg/L)
- \( C_t \) is the soil concentration (mg/kg)
- \( \rho_b \) is the bulk density (g/cm\(^3\))
- \( K_d \) is the partition coefficient (cm\(^3\)/g)
- \( n \) is porosity (dimensionless)

Compare theoretical pore water concentration to the solubility (\( S \)) or effective (\( S_e \)) of the compound of interest

Feenstra et al., 1991
US EPA guidance indicates that
1% effective solubility infers
the presence of DNAPL

\[
S_i^e = X_{mi} S_i
\]

Where:
- \( S_i^e \) is the effective solubility of component \( i \) in water
- \( X_{mi} \) is the mole fraction of component \( i \) in a given mixture
- \( S_i \) is the solubility of component \( i \) in water

Consider concentration trends with depth
Groundwater sampling downgradient of a DNAPL source zone

75% mass flux discharges through 5-10% plume cross-sectional area

(Guilbeault, et. al., 2005)
Emerging techniques

- Rapid site characterization tools (CPT-based)
  - Decreasing limit of detection
  - MIP-GCMS
  - DyeLIF for chlorinated solvent source zones
- Combined tools
  - FLUTe family
- Geophysical tools
  - Increasing resolution
  - Compound specific
- Real time data integration
  - Digital data capture
  - On-line GIS tools

Developed conceptual models for a range of DNAPLs in drift and bedrock
Ground Water Issue

Assessment and Delineation of DNAPL Source Zones at Hazardous Waste Sites

Bernard H. Kueper* and Kathryn L. Davies**

1.0 - Introduction

Groundwater contamination from classes of chemicals such as chlorinated solvents, polychlorinated biphenyls (PCBs), creosote, and cool oil is frequently encountered at hazardous waste sites (40, 41). These types of contaminants have low solubilities in water and have densities greater than that of water. Therefore, they can act as the subsurface in Dense, Non-Aqueous Phase Liquids (DNAPL) and have the potential to migrate as a separate liquid phase to significant distances below the water table in both unconsolidated materials and fractured bedrock. Because of the hydrogeological properties associated with DNAPL, they migrate through the subsurface as a very selective and dominant mechanism (31, 37, 39). Thus, the majority of DNAPL present in the subsurface may not be found immediately below the entry location and directly encountering DNAPL with conventional drilling techniques may be difficult.

Determining the presence or absence of a DNAPL is an important component of the conceptual site model and is critical to the proper selection of the remediation approach. Subsurface DNAPL acts as a long-term source for dissolve-phase contamination and determines the spatial distribution and persistence of contaminant concentrations within the vadose and saturated zones. Once it has been determined that DNAPL exists within the subsurface, subsequent characterization activities are typically conducted to better delineate the boundaries of the DNAPL source zone. The DNAPL source zone is the overall volume of the subsurface containing residual and pooled DNAPL. It should be recognized that there will be components associated with the distribution of the DNAPL source zone. In addition to the DNAPL, there may be significant amounts of contaminant mass that have diffused into the pore-water.

2.0 - Nature of the DNAPL Source Zone

Upgradient to the subsurface DNAPL, there will be mass-matched in the form of dissolved-phase hydrocarbons and pools of DNAPL, referred to as residual DNAPL, in saturated and unconfined aquifers referred to as residual DNAPL. Figure 1. Residual DNAPL is found both above and below the water table within the pathways of DNAPL migration, and typically occurs between 3% and 50% of pore space as pore fluids (20, 32) and in aquifer fractures (38). Residual DNAPL is trapped by capillary forces, and typically will not enter an adjacent monitoring well, even under the influence of aggressive groundwater pumping (6, 37).

Pools of DNAPL can occur above a regulatory barrier, which are typically layers and lenses of slightly less permeable material (Figure 1). Pools can also occur at any elevation in the subsurface and not just at the base of permeable zones. Absence of pooling above clay sediments and bedrock may be due to the presence of lensing features, bedding planes, joints and fractures which may allow the continued downward migration of the DNAPL. Pools represent a continuous distribution of DNAPL, and typically correspond to DNAPL saturations of between 30% and 90% of pore space in both porous media and fractures. The frequency of pool occurrence and the thickness of pools are increased by the presence of horizontal capillary barriers, lower DNAPL density, higher interfacial tension, and an upward component to groundwater flow (37, 38). The thickness of pools typically range from fractions of an inch to a few feet, depending on fluid and media properties (38) as well as the volume released. Because pools represent a connected distribution of DNAPL, the pooled DNAPL is subject to which is subject to migration through both vadose and saturated rock matrix and can be short-circuit flow along existing monitoring wells and fractures. In addition, pools may also be mobilized in response to changes in hydraulic gradients. The gradient required to mobilize a pool is a function of the DNAPL viscosity.
ITRC DNAPL Team Topics (2012-13)

- Conceptual models of DNAPL fate and transport
- The impact of geological and anthropogenic heterogeneities on DNAPL migration
- The effect of mobile and immobile pore spaces and the back diffusion issue
- Emerging methods to assess geology, DNAPL and associated dissolved phase distribution, including geophysics
- The role of analytical and digital modeling in DNAPL site characterization
- What managers should consider when reviewing site characterization plans
- Cost benefit assessment for DNAPL site characterization and sampling optimization